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LAKE SUPERIOR ORGANIC CARBON BUDGET

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Abstract—The organic carbon concentration of Lake Superior is discussed in terms of a simple mathematical model that treats the lake as a well mixed basin. Major sources, outflows, and biochemically mediated removal of organic carbon are analyzed in the time frame of yearly average values. Data on organic carbon concentrations of watershed drainage, rainfall, anthropogenic inflows and contributions from photosynthetic production are analyzed as are the removal of organics by biochemical oxidation and sedimentation. The long range projected effects of the major sources and sinks on the yearly average organic carbon concentration of the lake are described.

INTRODUCTION

Lake Superior is one of the world's largest bodies of freshwater. Its waters have unusually low concentrations of minerals, nutrients, and organics. There has been no substantial deterioration of water quality to date except for localized areas in the vicinity of major point sources of pollution. However, there is concern about the long range effects on the whole lake of the influx of nutrients and organics. This concern is partly prompted by the increasing population, and by industrialization of the Lake Superior drainage basin which is expected to lead to increasing pollution inflows.

Assessment of lake water quality has historically focused on the concentrations of nutrients and attendent algal growth and decay processes. However, it is now recognized that the concentration of organic carbon is a quantitative indicator of overall water quality that is useful for monitoring and detection of sources of pollution (Maier & Swain, 1977). Base line concentrations of total organic carbon (TOC) in Lake Superior have been determined. Open waters removed from sources of pollution average 1.1 mg l^{-1}. However, area wide increases in TOC were observed in the near shore areas that receive surface runoff from the drainage basin, and in the vicinity of point sources of pollution such as Duluth-Superior Harbor which has 12.6 mg l^{-1} of TOC. The long range effects of these area wide increases in TOC concentration on the whole lake have not been established but it is likely that there will be a gradual increase in TOC. The important unanswered questions are: how rapidly will TOC concentrations increase, what are the major contributing sources, and what is the lake's capacity for self-purification and flushing. To help answer these questions, data on Lake Superior basin waters were analyzed to identify and quantify the major sources and outflows of organic carbon and to evaluate the self purification processes in the lake. This paper describes the development and application of a mathematical model describing the carbon budget and elaborates on the magnitude of the fluxes and self purification process. Model predictions are used to assess the long range effects of the major sources and outflows on concentrations of organic carbon in the whole lake.

Material balance model

A simple mathematical model that treats the lake as a large well mixed basin was used to assess the effects of major inflows and outputs on the TOC concentrations of the whole water mass. Model calculations give insight on the relative importance of variables and allow projecting trends in concentration over long periods of time. Lake volume is represented by volume V. Inflows and outflows are characterized in terms of yearly average flow rates (Q), carbon concentration (C) and combined parameters as illustrated in Fig. 1.

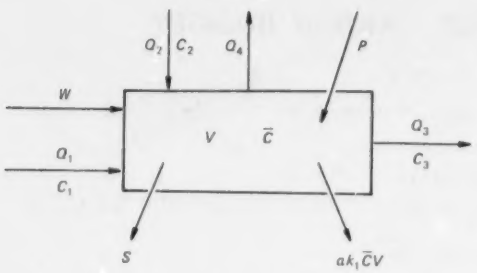
The generalized mass balance of organic carbon is described by equation (1):

$$Q_1C_1 + Q_2C_2 - Q_3C_3 - Q_4C_4 - \alpha k\bar{C}V + P \pm S + W = \frac{V\,d\bar{C}}{dt}. \quad (1)$$

The time rate of change of concentration of the lake is directly related to the summation of inputs and outputs. Each term of the equation is expressed in mg y^{-1}.

A year was chosen as the basic unit of time because preliminary analysis has shown that annual changes are small, thus the year unit is a convenient way of averaging out seasonal effects. Shorter time periods to model seasonal changes can be used, but require additional data on seasonal variations of the fluxes.

Fig. 1. Schematic of Lake Superior organic carbon material balance.



Q_1 = inflow from watershed drainage, 1 yr^{-1}.
Q_2 = inflow from rainfall on lake, 1 yr^{-1}.
Q_3 = outflow from lake, 1 yr^{-1}.
Q_4 = evaporation from lake, 1 yr^{-1}.
V = volume of lake, l
C_i = corresponding carbon concentration, mg l^{-1}
$\bar{C}$ = average carbon concentration in lake, mg l^{-1}.
k_1 = first order biochemical rate coefficient, $time^{-1}$.
α = ratio carbon to oxygen.
S = losses due to sedimentation.
P = production by photosynthesis.
W = inputs of carbon with wastewaters.

The terms S, P, and W are combined parameters expressed in terms of mg per year for the lake as a whole. For a well mixed basin of constant volume V, the outflow concentration C_3 can be replaced by the average lake concentration $\bar{C}$. The integrated form using fixed values for Q and the combined parameters P, S and W is shown as equation (2).

$$\bar{C} = m(1 - e^{-nt}) + \bar{C}_0 e^{-nt} \qquad (2)$$

where:

$$m = \frac{(Q_1C_1 + Q_2C_2 - Q_4C_4 + P \pm S + W)}{Q_3 + \alpha k_1 V}.$$

$$n = \frac{Q_3 + \alpha k_1 V}{V}$$

$\bar{C}o$ = initial concentration at $t = 0$.

Yearly average values for each parameter have been evaluated from published data on the hydraulic characteristics and water quality values of the watershed as discussed below.

Hydrological characteristics of Lake Superior

Lake Superior is a large body of water with a relatively long mean residence time of 189 yr (Rainey, 1967). The drainage area and shoreline are almost evenly divided between the U.S. and Canada (Table 1). Approximately 6% of the shoreline is considered to be influenced by industrial developments, but 60–80% of the shoreline is undeveloped. The Lake Superior watershed drainage averages 4.91×10^{10} m^3 yr^{-1}. Precipitation on the lake exceeds evaporation by a factor of 1.45. The yearly average outflow via the St. Mary's River is 6.96×10^{10} m^3 yr^{-1}.

Circulation patterns have been studied with a view to assessing the degree of dispersion of pollutants entering the lake from different sources (FWPCA, 1969). Water movement and rates of mixing are a function of turbulent mixing, lake currents, and stratification. For the lake as a whole, currents are the predominant mechanism of dispersion and movement. However, in summer, thermal stratification results in a well mixed epilimnion layer that encompasses less than 5% of the lake volume whereas the colder hypolimnetic water accounts for more than 95% of the water mass. For most of the year, the lake is not stratified and wind activated rates of circulation are sufficiently rapid so that persistent pollutants entering the lake are dispersed and become an integral part of the whole lake (FWPCA, 1969).

Carbon influx from the watershed

Drainage from the watershed is a large potential source of organic matter entering the lake continuously. Yearly inflow of TOC is expressed in terms of Q_1C_1, where Q_1 is the yearly average flow in 1 yr^{-1}, and C_1 is the average carbon concentration in mg l^{-1}. Q_1C_1 represents the summation of yearly average inputs of all n tributaries feeding into Lake Superior:

$$Q_1C_1 = \sum_j^n \int_0^t q_j c_j \, dt.$$

Table 1. Characteristics of the Lake Superior basin.

	Total	U.S.	Canada	Minnesota
Lake volume, m^3	1.25×10^{13}	—	—	—
Total basin, m^2 (includes lake)	2.08×10^{11}	0.98×10^{11}	1.1×10^{11}	0.21×10^{11}
Land surface, m^2	1.26×10^{11}	0.43×10^{11}	0.82×10^{11}	0.16×10^{11}
Shoreline, mainland, m	4.8×10^6	2.3×10^6	2.5×10^6	0.3×10^6
Percent undeveloped, %	73	62	84	—
Percent industrial, %	6	5	7	—
Tributary flows, m^3yr.	4.91×10^{10}	—	—	0.67×10^{10}
Outflow, m^3 yr^{-1}.	6.96×10^{10}	—	—	—
Precipitation on lake, m^3 yr^{-1}.	6.60×10^{10}	—	—	—
Evaporation from lake, m^3 yr^{-1}.	4.55×10^{10}	—	—	—
Water surface m^2	0.82×10^{11}	0.55×10^{11}	0.27×10^{11}	0.56×10^{10}

References: FWPCA, 1969, Minn. Dept. Conserv., 1966; Minn. Dept. Conserv., 1964, Upper Lakes Ref., 1976.

Table 2. Summary of organic carbon values for selected Lake Superior tributaries

River basin characteristics	St. Louis partly industrialized—some lakes	Baptism sparsely settled rapid runoff	Pigeon sparsely settled ponded
Drainage area m^2	8.9×10^9	0.4×10^9	1.6×10^9
Flows, $m^3\ s^{-1}$			
Average monthly	85	6	18
Maximum monthly	213	17	63
Minimum monthly	33	0.8	5
Organic carbon concentrations, $mg\ l^{-1}$			
Average month	22	11	9
Maximum	36	18	17
Minimum	12	6	5
Organic carbon transported, $g\ s^{-1}$			
Average	2130	63	187
Maximum	5480	245	565
Minimum	1070	4	27
"Runoff coefficient"*,			
Grams m^{-2}-year	7.5	5.0	3.7
Equivalent TOC, $mg\ l^{-1}$	18.9	12.6	9.3

* Organic carbon transported per unit of drainage area yr^{-1}.

Integral $q_j c_j$ denotes the yearly average of the jth stream and incorporates seasonal variations in flow and concentration. Flow records for the major tributaries of the Superior drainage basin are available from the United States Geological Survey and its Canadian counterpart. However, monthly data on carbon concentrations are limited to selected tributaries surveyed by the Minnesota Pollution Control Agency (Maier *et al.*, 1975a, b), and averaged values from some 21 Canadian Rivers (Upper Lakes Ref., 1974). Analysis of the data from 20 tributaries shows that the concentration of organic carbon varies both seasonally and geographically due to differences in the geological, hydrological and climatic characteristics of watershed. The results for 3 representative watersheds are summarized in Table 2. The St. Louis River basin was chosen because it is partly industrialized and receives considerable inflows of organics from anthropogenic sources (Minn. Dept. Conserv., 1964). The Baptism River basin is a sparsely populated region with steep slopes and has rapid runoff of surface waters. Low flows are sustained from ground water seepage. The Pigeon River basin is more typical of the northern ponded areas that derive sustained flow of surface water impoundments (Minn. Dept. Conserv., 1966). Monthly averages and maximum–minimum values for flow and TOC concentrations are listed in Table 2. Highest concentration of TOC occur in the St. Louis River which receives large quantities of organic matter from industrial plants. Average TOC concentrations in the Baptism and Pigeon River are at the same level. However, the flow per unit area of drainage basin is higher in the steeply sloped Baptism River. These differences are illustrated by comparison of the calculated Surface Runoff Coefficients, SROC, for organic carbon which is highest for the St. Louis River basin, $7.5\ g\ m^{-2}\ y$ and lowest for the Pigeon River basin, $3.7\ g\ m^{-2}\ y$. The mean organic carbon concentration (TOC) for the Baptism River is $11\ mg\ l^{-1}$ for the average month and $12.6\ mg\ l^{-1}$ based on average flow. This is in close agreement with the average value of $12\ mg\ l^{-1}$ TOC reported for 21 Canadian Rivers in the Lake Superior watershed (Upper Lakes Ref., 1974). For purposes of modelling, the influx of organic carbon was calculated from SROC and the total drainage area of the watershed. Using the lower value of $3.7\ g\ m^{-2}/y$, the calculated yearly influx of organic carbon to the lake is $4.6 \times 10^{14}\ mg\ y^{-1}$. This value represents a "low estimate" because it treats the whole basin as an undeveloped region. A more realistic value is obtained by using the median runoff coefficient of $5\ g\ m^{-2}/y$ which predicts an influx of $6.3 \times 10^{14}\ mg\ y^{-1}$. If the whole watershed approaches industrial and population densities typified by the St. Louis River watershed, influx of organic carbon would increase to 9×10^{14} $mg\ y^{-1}$.

Outflow

Flow from Lake Superior is regulated by the St. Mary's River control works to maintain a constant lake level. Outflow (Q_3) averages $6.96 \times 10^{10}\ m^3\ y^{-1}$. (Table 1). Withdrawals for consumptive uses by industry and municipalities are negligible. The outflow of carbon is therefore defined by $Q_3\bar{C}$ where $\bar{C}$ replaces the outlet concentration because the lake is modelled as a well mixed basin.

Evaporation and atmospheric exchange

Evaporation losses of water from the lake surface (Q_4) are reported to be $4.55 \times 10^{10}\ m^3\ y^{-1}$ (Table 1).

Loss of organic matter by evaporation is likely to be very small because most of the aquatic organic substances consist of relatively large, low volatility molecules that have physical chemical characteristics similar to fulvic materials from soil. Laboratory stripping with nitrogen had no effect on TOC. The concentration term C_4 was therefore set equal to zero.

Rainfall

Precipitation on Lake Superior ranges from 50 to 75 cm y^{-1} which produces an average yearly inflow (Q_2) of 6.6×10^{10} m^3 (Table 1). Precipitation and dry fallout are recognized as important mechanism by which soluble and particulate matter are removed from the atmosphere. Almost all trace substances present in the atmosphere are also present in precipitation, but the relationship between concentration in the atmosphere and precipitation is dependent on a variety of atmospheric conditions that include such factors as intensity of rainfall, mechanism and rate of drop formation, size of drops, elevation, and the physical–chemical characteristics of air pollutants (Junge, 1963). Assessment of the chemical composition of rain and snow is further complicated by the effects of dry fallout of particulate matter from the atmosphere.

Only in a few cases has the organic content of rainfall and snowfall been measured (Table 3). Measurements of organic carbon in precipitation in Sweden range from 0.8 to 3.4 mg l^{-1} (Neumann *et al.*, 1959 cited by Junge, 1963). Concentrations of organic carbon in rainfall in Hawaii range from 2 to 12 mg l^{-1}, and an average of 8 mg l^{-1} was found near Washington (Swinnerton *et al.*, 1971). Organic carbon measurements on spot samples of rainfall in the Minneapolis area range from zero in the suburbs to 9.0 mg l^{-1} in the city. Estimates of organic carbon concentrations based on ignition losses of the total solids in precipitation in Nova Scotia are 1.3 and 6.5 mg l^{-1} for snow and rain respectively (Herman *et al.*, 1957). Since there are no published data on TOC levels in precipitation over Lake Superior, the influx of carbon from this source was estimated from the range of values listed in Table 3. A value of 1.0 mg l^{-1} was used as representative of unpolluted atmospheric conditions; 3 mg l^{-1} as representative of average conditions and 9.4 mg l^{-1} as an estimate of the upper limit that would be typical of industrialized–populated regions. The corresponding yearly influx of carbon for the whole lake is 6.6×10^{13}, 2.0×10^{14} and 6.3×10^{14} mg y^{-1} respectively.

Biochemical oxidation

Most naturally occurring organic materials are susceptible to biochemical oxidation and are ultimately converted to carbon dioxide and water. However, the rates of oxidation of aquatic organic materials are very slow (Kim, 1976; Reed, 1971). Oxidation is conventionally measured in terms of oxygen uptake and reported as biochemical oxygen demand (BOD). BOD rates are expressed in terms of the deoxygenation coefficient k_1. There is no direct information on the rates of biochemical oxidation of aquatic organic substances from Lake Superior. However, it is reasonable to assume that the organic materials in Lake Superior are similar to, but more refractory than those in the Upper Mississippi River basin for which data are now available. The long residence time in Lake Superior is conducive to the accumulation of refractory organic substances because the more biodegradable organic materials are probably oxidized shortly after they enter the lake. Laboratory studies on organic matter from the Mississippi River show at least the initial phase of oxygen uptake can be approximated by classical BOD kinetics, i.e. the rate of oxidation is proportional to the concentration of organic matter remaining. However, there are indications that rates of oxidation are independent of organic carbon concentrations in situations where TOC concentrations are very low and the residue organics are refractory. Deoxygenation coefficients for Mississippi River organic materials range from 0.1 day^{-1} in short term tests (20 days), which mineralize less than 20% of the carbon, to 0.03 day^{-1} in long term tests (100 days), which mineralize up to 50% of the carbon. It is estimated that complete mineralization requires at least 260 days and the rate ceofficients become correspondingly smaller. Estimates of k_1 values for complete oxidation based on Mississippi

Table 3. Organic carbon concentration in rainfall

Location	Concentration, mg l^{-1}	Reference
Sweden	0.8–3.4	Junge, 1963
Hawaii	2–12	Swinnerton, 1971
Washington	8	Swinnerton, 1971
Minneapolis–St. Paul	0–9	Herein
Nova Scotia	1.3–6.5	Hermann, 1957
Estimates of organic carbon concentration used for this study		
	mg l^{-1}	
Low	1	
Base case	3	
High	9.4	

† Based on 50% of ignitions loss of solids collected as precipitation.

Table 4. Deoxygenation coefficients for aquatic organic materials

Temperature °C	20	6†
Mississippi River water		
k_1, day^{-1}		
20 day test	0.10	0.016
100 day test	0.03	0.005
ultimate BOD*	0.003–0.01	0.0005–0.0016
αk_1, day^{-1}	—	0.0001–0.0003

* Extrapolation based on carbon measurements.
† Temperature adjustment calculated from $k_{1,t} = k_{.20}\ 1.135^{T-20}$.

River aquatic organic substances are shown in Table 4. Values in the second column have been adjusted to 6°C to reflect the lower temperatures that prevail in Lake Superior. The overall rate of organic carbon removal is given by $\alpha k_1 \overline{C}$; α is a proportionality coefficient that converts oxygen (BOD) to organic carbon (TOC) consumption. It was found to have a value of 0.2 in the study on Mississippi River water. This value is substantially lower than the TOC/BOD ratios usually reported for domestic wastes and may reflect the fact that aquatic organic materials are in a more reduced form. The low value of α may also be due to incomplete oxidation of refractory constituents which results in oxygen utilization without equivalent carbon dioxide release. For purposes of modelling, αk_1 values ranging from 0 to 0.001 day^{-1} were used.

Photosynthetic production (P)

The interchange of carbon from the inorganic to the organic compartment by photosynthesis is a crucial aspect of lake water quality. Fortunately, the rates of photosynthesis in Lake Superior are low. The total mass of particulate organic carbon fixed by photosynthesis is estimated in the range 1.5–1.8 × 10^{12} g y^{-1} (Parkos, 1969). If this were dispersed throughout the whole lake, it would be equivalent to an increase in carbon concentration of 0.12–0.14 mg l^{-1}. If photosynthetic production were dispersed only in the epilimnion (upper 5%) during summer stratification, the total increase in organic carbon would be some 20-fold larger and easily detectable by TOC measurements. However, the accumulation of plankton biomass in surface waters depends on the combined effects of the rates of production, biochemical oxidation, and sedimentation. Plankton biomass is susceptible to biochemical degradation and oxidation by bacteria. The rate and mechanism of decay of algal biomass has been studied using dead *Scenedesmus sp.* cells in the presence of microflora extracted from lake mud and water (Otsuki, 1972). Particulate algal biomass was metabolized into new bacterial particulate cell mass, dissolved organic materials (passing through 0.45 μm filter), carbon dioxide, and water. High rates of degradation prevailed for the first 5 days. Dissolved organic carbon (DOC) was released into the solution to the extent of 7% of the initial carbon biomass. However, the concentration decreased continually after the first 100 days. It appears that DOC is an intermediate metabollic product that undergoes complete mineralization in less than one year. Extrapolation of this information to the Lake Superior organic carbon budget suggests that there would be no net yearly input of DOC from this source. Measurements of particulate organic matter showed that approximately 45% of the particulate organic carbon disappeared during the first five days. By the 50th day, particulate carbon (including newly formed bacterial cell mass) accounted for less than 30% of the original particulate matter. The residual particulate matter appeared to be largely cell wall material that was resistant to bacterial attack. Further incubation for an additional 175 days reduced particulate carbon to 25%. Extrapolation of these data to the Lake Superior carbon budget indicate that the net yearly input of particulate organic carbon from algal biomass is likely to be less than 25% of the original algal carbon mass. Zooplankton predation also contribute to the decay of algal biomass; however, data available from other model studies suggest that this is not an important factor (Maier, 1975c).

Sedimentation

The importance of sedimentation in removing algal biomass particulates from the upper water layers is well established (Smayda, 1970; Higuchi, 1975). In Lake Ontario measured settling velocities of particulate carbon varied from −0.4 to +2.0 m day^{-1} (Burns & Pashley, 1974). There appeared to be an increase in settling velocity with depth to an intermediate zone between 50–100 m, thereafter settling velocities decreased with depth. Sedimentation of particulates, therefore, serves to disperse organic materials vertically throughout the water mass and may result in accumulation in the sediments. The ultimate fate of particulates after they settle out of the epilimnion is a matter for speculation. There are no indications that organic matter is accumulating in hypolimnetic waters and/or the sediments. This suggests that there is a continuous turnover of organics as a result of biological oxidation and upwelling. For purposes of model calculations, sedimentation will be considered as a dispersion mechanism for particulates, but not as a mechanism for removal of organics from the lake water mass as a whole.

Considering the overall effects of photosynthesis, the decay of algal biomass and the effects of sedimentation, the net yearly accumulation of organics in the Lake Superior water mass is probably negligible. To the extent that yearly mineralization of the annual crop of phytoplankton is incomplete and not lost to sediments, the residues will contribute to the aquatic carbon pool. The upper limit on net yearly contributions from this source can be estimated from the information on productivity and decay rates. Using a

yearly average production rate of 1.6×10^{12} g carbon y^{-1} with a maximum residue of 25%, the net yearly addition to the aquatic carbon pool would be 0.4×10^{15} mg for Lake Superior. For purposes of model calculations, the net yearly input will be assumed to be in the range of zero to 0.4×10^{15} mg y^{-1}.

Inflow of anthropogenic organic wastes (W)

Organic wastes from man related activities enter the lake as direct inflows of industrial and municipal wastes, and indirectly through the loadings of such wastes into tributary streams. The indirect inflow of organic carbon from industrial and municipal sources via the St. Louis River has been discussed. This material is responsible for the higher runoff coefficient. The direct inflow from municipal and industrial sources to Lake Superior has been estimated to be 4250 and 196,000 kg BOD day^{-1} respectively (Upper Lakes Ref., 1976). This is equivalent to an added influx of $3.9–7.1 \times 10^{13}$ mg y^{-1} of organic carbon depending on the nature of the waste.

DISCUSSION

Model calculations were made using equation 2 to project the effects of each major flux on the year to year average organic carbon concentration in Lake Superior. Figure 2 illustrates the effects of watershed drainage for progressively larger values of SROC as the only source of organic carbon and without biological oxidation. Lake concentration increases from its present level of 1.1 mg l^{-1} for all values of SROC larger than 0.4 g m^{-2} y.Using the medium runoff coefficient of 5 g m^{-2} y (equivalent to an inflow concentration of 12.6 mg l^{-1}) the model predicts a gradual increase in TOC of 0.5 mg l^{-1} in the first 10 y; concentrations would ultimately reach an equilibrium level of 9.5 mg l^{-1}. The yearly increases in concentration are small, but the cumulative effect over tens of years could change water quality dramatically. At a lower runoff coefficient of 3.7 g m^{-2} year, typical of undeveloped areas, the trend is similar, but the increase is less than 0.3 mg l^{-1} in the first 10 y. Such small increases can not be detected with present analytical techniques. A run off coefficient of 7.4 g m^{-2} y, which is representative of industrially developed regions and includes anthropogenic inputs (wastewaters and urban runoff) would double the present concentration in 16 y and increase TOC levels to 6.5 mg l^{-1} in 100 y. Estimates of the direct influx of anthopogenic organic carbon range from 3.9×10^{13} to 7.1×10^{13} mg y^{-1} (Upper Lakes Reference Group, 1974). This is a relatively small fraction of the total influx from runoff which ranges from 4.6×10^{14} to 9.45×10^{14} mg y^{-1} for runoff coefficients of 3.7 and 7.5 g m^{-2} y respectively. Furthermore, some of the anthropogenic inflows have already been accounted for in the higher runoff coefficient that was calculated for the industrialized–populated region drained by the St. Louis River. For purposes of model calculations and interpretation, the influx of anthropogenic organic matter was, therefore, considered to be included in the runoff coefficient.

If the lake were stratified so that the influx of TOC is dispersed in the epilimnion only, the effects of surface inflows would become apparent more quickly as shown in Fig. 3. Using a surface runoff coefficient of 5 g m^{-2} y (no biological oxidation) TOC, after 10 y, would reach 1.5, 1.9, 3.0, 4.5 mg l^{-1} for volume fractions of 1.0, 0.5, 0.2, 0.1 respectively. The ultimate concentration in the mixed volume would be the same in all cases. It is unlikely that the unmixed portion of the lake would remain compartmentalized over extended periods as long as a decade. Thus, these calculations should be viewed as an upper limit of the effects of stratification or compartmentalization. However, compartmentalization would have to be considered for modeling seasonal rather than year to year effects.

Rainfall and dry fallout contribution to the carbon

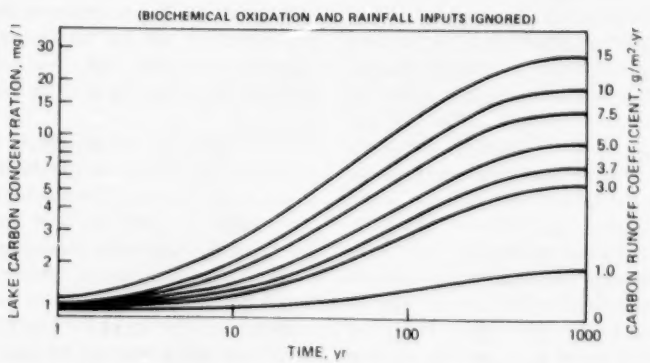


Fig. 2. Effect of carbon runoff on lake carbon concentration.

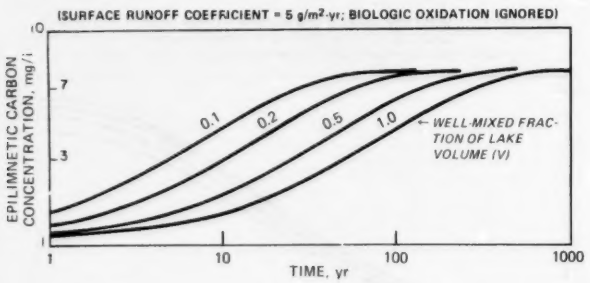


Fig. 3. Effect of stratification on Lake Superior carbon content.

budget is likely to be somewhat less than that from surface runoff. The combined effects of carbon influx from rainfall and surface runoff (SROC = 5 g m^{-2} y) are illustrated in Fig. 4. At a concentration of 1 mg l^{-1} TOC in rainfall, the effect on lake water would be negligible. At 3 mg l^{-1} the effect is still small, but its cumulative effect would be significant after 10–20 y. A rainfall concentration of 9.4 mg l^{-1} TOC, which is typical of precipitation in the vicinity of industrialized areas, would double the present lake concentration in 12 y compared with 26 y for surface runoff as the only carbon influx; the 100 y concentration would increase to 8.3 mg l^{-1} versus 4.5 mg l^{-1} for surface runoff alone. The potential importance of rainfall input is illustrated by the fact that 9.4 mg l^{-1} TOC in rainfall has essentially the same effect on lake carbon content as a runoff coefficient of 5 g m^{-2} y. Another method of comparing the effects of rainfall and surface runoff is to note that 1 mg l^{-1} TOC in rainfall is equivalent to 1.3 mg l^{-1} in surface runoff.

Analysis of precipitation data shows that open areas removed from large sources of atmospheric pollution are likely to have low TOC concentrations, less than 3 mg l^{-1}. These organics originate from natural sources, e.g. forests and vegetative decay. Higher TOC concentrations (9–12 mg l^{-1}) are not uncommon in regions that are affected by industrialization. The Lake Superior region is considered to be sufficiently far removed from major industrial development so that precipitation is likely to have low TOC concentrations and an average value of 3 mg l^{-1} was used for subsequent model studies.

The net yearly increase in TOC due to photosynthetically produced organic carbon (not remineralized nor lost to sediments) depends on gross productivity and decay rates. Figure 5 illustrates the effect of accumulating from 0 to 25% of the gross productivity of 1.6×10^{15} mg y^{-1}. The concentration curves show cumulative effects of influx from surface runoff, rainfall and photosynthesis. For 25% residue, TOC concentrations would increase from 1.7 to 2.0 mg l^{-1} in 10 y. The influx of carbon from photosynthesis would have the same effect as increasing SROC by 3.2 g m^{-2} y. If only 10% of the yearly gross productivity is added to the organic pool, the effect on TOC is small, approximately 0.1 mg l^{-1} in 10 y. However, if gross productivity of the lake were to increase substantially due to excessive fertilization, the effects could become significant even at the 10% residue level.

Mineralization of organic carbon by biological oxidation is probably the most important single factor with regard to the steady state carbon concentration in Lake Superior. The effects of biological

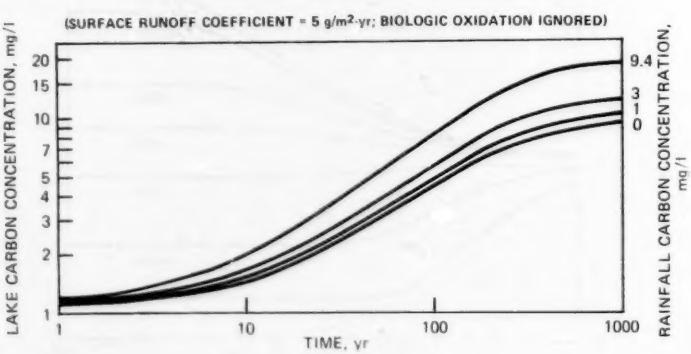


Fig. 4. Effect of rainfall carbon content on Lake Superior.

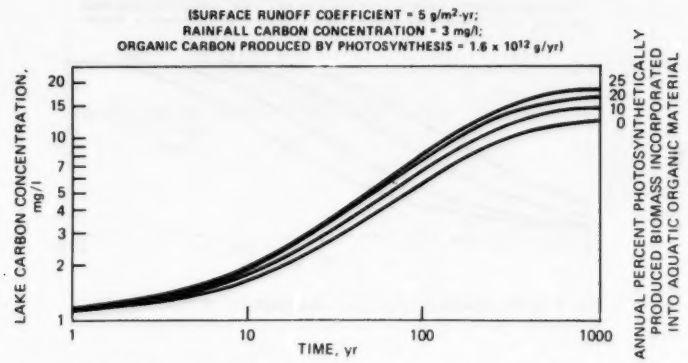


Fig. 5. Effect of photosynthetic production on concentration of organic materials.

oxidation are illustrated in Fig. 6. For αk_1 values in the 0.0001–0.0002 day^{-1} range, TOC concentrations would remain essentially unchanged because the yearly input of organic matter is mineralized in the course of each year. A ten-fold decrease in αk_1 to 0.00001 day^{-1} makes the effect of biological oxidation negligible. Under these conditions TOC after 10 y is 1.6 versus 1.7 $mg\,l^{-1}$ without biological oxidation. Extrapolation of the biological oxidation coefficients measured in Mississippi River organics (Table 4) are in the 0.0005–0.001 day^{-1} range. If Lake Superior decay rates were of this magnitude, Fig. 6 shows that TOC concentrations would decrease from the present levels of 1.1 $mg\,l^{-1}$ to 0.35 and 0.18 $mg\,l^{-1}$ respectively. The predicted drop in concentration indicates that biological oxidation rates are higher than necessary for oxidizing the yearly influx rate, thereby reducing yearly average concentration levels in the lake. The total mass of carbon mineralized is modeled by the term $\alpha k_1 \bar{C} V$. If this term exceeds the yearly influx, then the lake TOC concentration $\bar{C}$ drops until a new steady state concentration is obtained, at which $\alpha k_1 \bar{C} V$ is in balance with the influx. There is no reason to believe that TOC levels in Lake Superior are decreasing under present conditions and it seems reasonable to conclude that lower biological oxidation rates prevail. Lower rates of biological degradation in Lake Superior may be due to the more refractory nature of the organic substances compared to the organic substances in river water. River water has a larger proportion of organic matter of recent origin which probably accounts for higher αk_1 values. This is consistent with the report that deep oceanic waters (long residence time) contain approximately 0.6 $mg\,l^{-1}$ of organic carbon that is very refractory to biological degradation (Barber, 1968).

SUMMARY–CONCLUSION

Analysis of the organic carbon budget for Lake Superior shows that watershed runoff, precipitation,

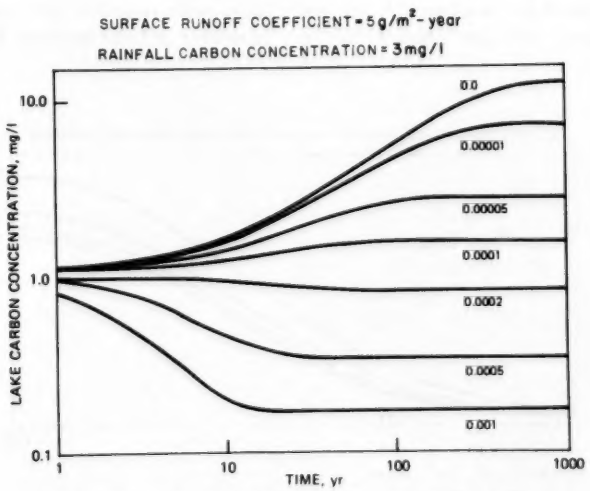


Fig. 6. Effect of biological oxidation on carbon concentration.

and *in situ* photosynthetic production are major sources of inflow that could ultimately lead to significant deterioration of water quality. Influx of organic matter from watershed drainage has been described in terms of the surface area and a surface runoff coefficient (SROC) that is characterized by topographical–hydrological factors and the level of industrial–urban activity. The St. Louis River watershed has the highest SROC ($7.5\,g\,m^{-2}\,y$) which reflects the influx of industrial and urban wastes. SROC values of undeveloped watersheds range from 3.4 to $5.0\,g\,m^{-2}\,y$. Influx of organic carbon from the atmosphere in the form of rainfall or dry fall-out depends on atmospheric conditions. Since there are no published data on the organic concentrations in rainfall over Lake Superior, a range of TOC values deduced from other sources have been used for model calculations. Open areas such as Lake Superior which are removed from large sources of atmospheric pollution are likely to be low ($0–3\,mg\,l^{-1}$). Rainfall TOC concentrations in the $0–3\,mg\,l^{-1}$ range would have a small effect compared to runoff influx. However, a level of $9.4\,mg\,l^{-1}$, which is more typical of industrial areas, would increase the carbon burden of the lake by an amount equivalent to the tributary runoff associated with an SROC of $5\,g\,m^{-2}\,y$.

The net yearly accumulation of organic carbon from photosynthetic production is undoubtedly small because gross productivity for the lake as a whole is low. Seasonal and localized photosynthetic production in the epilimnion may result in measurable increases in concentration depending upon rates of decay and sedimentation. Nevertheless, most of the biomass (<75%) will be remineralized within the course of the year, and net yearly contributions to the aquatic pool are likely to be small. As an upper limit estimate, if 25% of the new biomass were added to the pool, the net effect would be equivalent to the quantity of organic carbon entering by surface runoff at a rate of $3.2\,g\,m^{-2}\,y$.

Removal of organic carbon occurs by two principal means: (1) outflow of water from the lake, and (2) biological oxidation that mineralizes organic carbon to carbon dioxide. Direct outflow is proportional to the yearly mean flow rate and average TOC concentration of the lake. Removal of organic materials by biological oxidation is probably the single most important factor in the overall carbon budget. Model calculations show that the steady state TOC concentration is quite sensitive to rates of oxidation. High rates would maintain low TOC concentrations regardless of carbon influx. A ten-fold lower rate makes biological oxidation a negligible factor. Analysis of the model calculations suggest that rates of oxidation are much slower than the values measured for aquatic organic substances from Mississippi River water. Removal of organic particulates by sedimentation with attendent accumulation in the sediments is a removal mechanism in eutrophic lakes; it is unlikely to be a major factor in oligotrophic Lake Superior.

The analysis of the Lake Superior carbon budget provides a useful framework for evaluating the effects of the major fluxes of organic carbon even though simplifying assumptions have been made. Perhaps the most important conclusion is that there are large yearly inflows of organic matter whose effect on TOC concentration in the lake are muted because of the dilution effect in the large lake volume. However, the dilution effect can be misleading because small yearly increases that are difficult to verify experimentally could herald large long term changes. For example, if industrialization doubles runoff coefficients, the yearly increase in TOC would be less than $0.05\,mg\,l^{-1}$, but long term effects could be dramatic with lake concentration reaching gross pollution levels ($5\,mg\,l^{-1}$) in less than 70 y. Detection of small incremental changes in TOC from year to year will require extensive sampling and use of refined analytical methods. The possibility of using modified TOC measurements in conjunction with analytical determinations of the chemical and biochemical characteristics of the organic materials should be explored.

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